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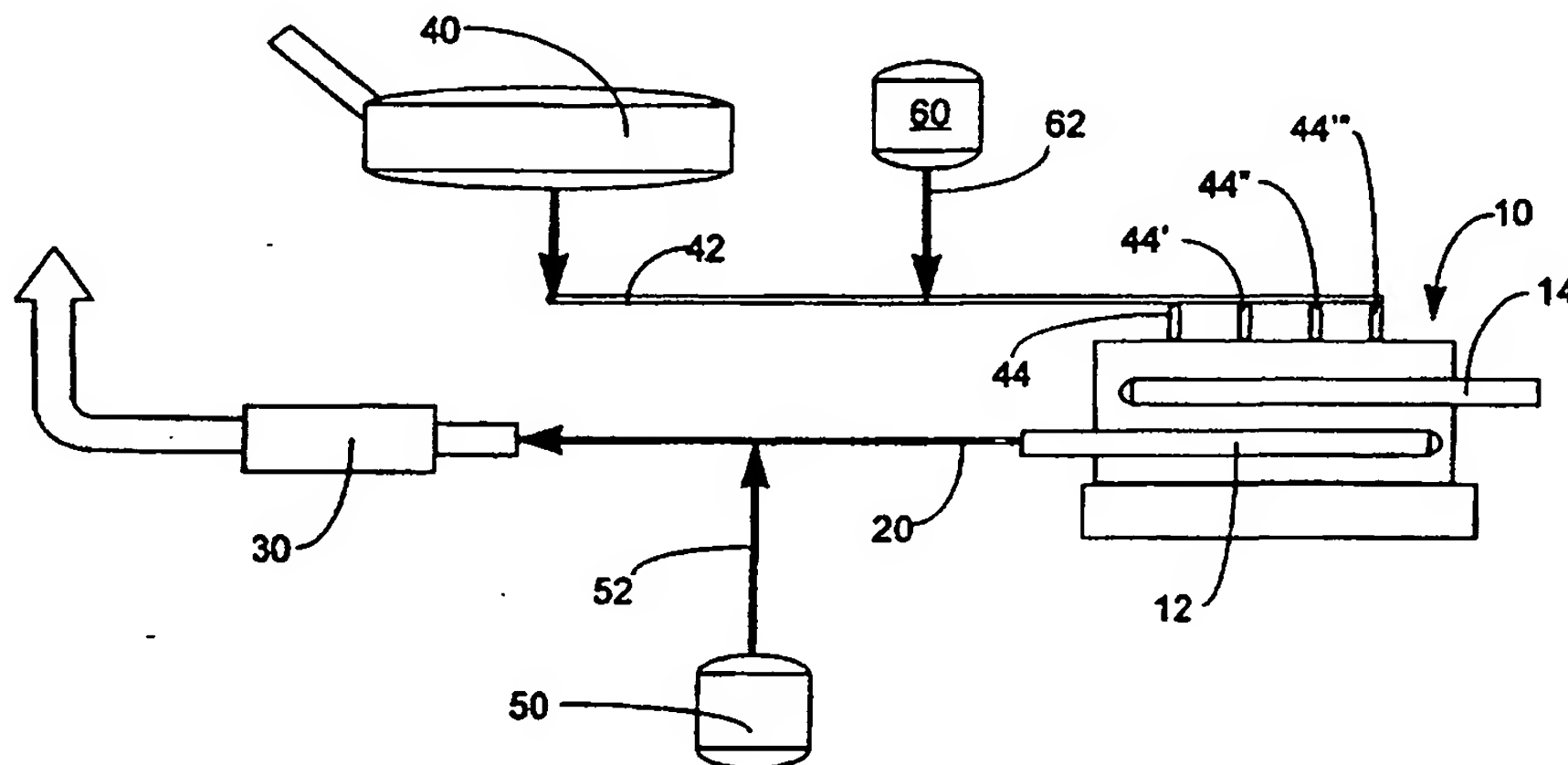
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(54) Title: METHOD AND APPARATUS FOR REDUCING HARMFUL EMISSIONS FROM A DIESEL ENGINE BY POST COMBUSTION CATALYST INJECTION



## (57) Abstract

Emissions of pollutants from diesel engines (10) are reduced by a regimen for catalytically treating engine exhaust and, preferably, also the combustion of the fuel. The balance point of a diesel trap (30) is reduced to permit more efficient regeneration, preferably self-regeneration, while also reducing emissions of carbon monoxide and hydrocarbons by a combination of mechanical devices and fuel additives. The regimen requires the introduction of from 0.05 to 1 ppm of a platinum group metal catalyst (based on the volume of fuel combusted) into the particulates, by introducing at least half of the platinum group metal catalyst (50) directly into the hot exhaust gases (52, 20). Preferably, the platinum group metal catalyst is employed with a combustible organic liquid to aid in either progressively loading the trap (30) with the combustible organics or to combust in the hot combustion gases to facilitate burning of the particulates on the trap (30) for more effective regeneration. The judicious selection and use of an auxiliary catalyst metal (e.g., copper), preferably adding at least half of its total to the fuel as a fuel additive, is a preferred part of the regimen to achieve the lowest trap balance point.

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## DESCRIPTION

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### METHOD AND APPARATUS FOR REDUCING HARMFUL EMISSIONS FROM A DIESEL ENGINE BY POST COMBUSTION CATALYST INJECTION

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#### Technical Field

15       Despite the relative economy and thermodynamic efficiency of diesel engines, more widespread use will be deterred until a reasonable solution is found to their tendency to discharge pollutants. The invention provides solutions to this problem by the discovery of a regimen for catalytically treating engine exhaust and, preferably, also the combustion  
20       of the fuel. The invention enables the balance point of a diesel trap to be reduced to permit more efficient regeneration, preferably self-regeneration, while also reducing emissions of carbon monoxide and hydrocarbons.

      The economical and the ecological advantages offered by diesel  
25       engines will not be fully realized until technology becomes available to reduce all pollutant species found in diesel engine exhaust. These pollutants include carbon monoxide (CO), unburned hydrocarbons (HC), particulates, and nitrogen oxides (NO<sub>x</sub>). The particulates are typically reduced by equipping diesel engines with particulate traps, mounted in the  
30       exhaust stream, to "trap" or otherwise collect particulates from the exhaust to prevent their emission to the atmosphere. Traps alone cannot handle all of the emissions, and it has been difficult to find the right combination of pollution control measures because the various forms of pollutants seem to be interrelated.

MISSING UPON TIME OF PUBLICATION

As diesel traps perform their work of collecting the particulates, back pressure increases across the trap until it must be replaced or regenerated. In some exhaust systems, regeneration is effected by burning the particulates in place on the trap by the use of auxiliary heaters. This is not fully effective because exhaust temperatures are not continuously high enough for regeneration, and the addition of electric heaters is not practical for most applications.

Various fuel and exhaust additives have been proposed to reduce one or more pollutants or to solve a problem related to diesel traps; however, the achievement of lower emissions of unburned hydrocarbons and carbon monoxide, while controlling particulates over reasonable periods of time and at catalyst levels that do not adversely affect trap structural and functional integrity, continues to present a technical challenge.

### Background Art

Diesel particulates, their effect and control, are the focus of concern and controversy. Their chemistry and environmental impact present complex issues. Very generally, diesel particulate matter is principally solid particles of carbon and metal compounds with adsorbed hydrocarbons, sulfates and aqueous species. Among the adsorbed species is a soluble organic fraction (SOF) which contains aldehydes and polycyclic aromatic hydrocarbons (also called PAH's). Some of these organics, as well as the particulates themselves, have been reported to be potential carcinogens. Unburned hydrocarbons are related to the characteristic diesel odor and include aldehydes such as formaldehyde and acrolein. The adsorbed hydrocarbons, like the carbon monoxide and gaseous unburned hydrocarbons, are the products of incomplete combustion.

It is not just organics which are of concern, all particulates are subject to question. In one study, diesel particulates were tested along side  $\text{TiO}_2$  and carbon without any adsorbed hydrocarbons. (U. Heinrich, *et al.*,  
5 "Tierexperimentelle Inhalationsstudien Zur Frage der Tumorinduzierenden Wirkung von Dieselmotorabgasen und zwei Teststauben", *Ökologische Forschung BMFT/GSF*, Munich, 1992) The reporters determined that all species tested showed carcinogenic tendency. Until further work clarifies this matter, it would be prudent to look for systems which could control all  
10 particulates -- regardless of composition.

For diesels, the use of particulate traps appears essential, but there is a strong need to improve them -- resulting in a great deal of research and a great number of patents and technical publications. The traps are typical-  
15 ly constructed of metal or ceramic and are capable of collecting the particulates from the exhaust and withstanding the heat produced by oxidation of carbonaceous deposits which must be burned off at regular intervals. Increased particulate collection will raise the rate of back pressure buildup. Often, burning particulates will increase the emissions of carbon  
20 monoxide and gaseous hydrocarbons. The various pollutants seem to be interrelated, with reduction of one sometimes increasing levels of another.

Trap regeneration by burning particulates would be advantageous if it were self regulating and did not increase gas phase pollutant emissions.  
25 Regeneration could occur by itself if the operating temperature of the trap were sufficiently high. However, in the typical situation, the exhaust temperature is not constantly high enough, and secondary measures such as electrically heating to raise the trap temperature, using a catalyst to reduce the combustion temperature, supplemental burners, and exhaust gas  
30 throttling have been attempted. Electrical heaters create intense loads on

batteries, most needed at lower power settings where the electrical output is also low. Supplemental heaters and exhaust gas throttling can lower efficiency.

5 In "Control of Diesel Engine Exhaust Emissions in Underground Mining", 2nd U. S. Mine Ventilation Symposium, Reno, Nevada, Sept. 23-25, 1985, at page 637, S. Snider and J. J. Stekar report that precious metal catalysts in a catalytic trap oxidizer and a "catalyzed Corning trap" were effective in the capture of particulate matter. The report also discussed several other ap-  
10 proaches, including the use of a fuel additive containing 80 ppm manganese and 20 ppm copper to reduce the regeneration temperature of the trap. Moreover, high levels of metallic additives can cause traps to plug.

15 Traps are reasonably effective for controlling particulates, but uncatalyzed traps can increase carbon monoxide and catalyzed traps can increase the discharge of  $\text{SO}_3$  (adding to the weight of particulates) and suffer from other problems. For example, see Niura, Ohkubo and Yagi, "Study on Catalytic Regeneration of Ceramic Diesel Particulate Filter", SAE  
20 Technical Paper Series No. 860290, February, 1986. Traps, of course, don't reduce  $\text{NO}_x$  and efforts made to control  $\text{NO}_x$  must be carefully selected or the result might be to further increase particulates or other products of incomplete combustion.

25 The above Niura, *et. al.*, paper reports on several investigations of regenerating diesel particulate traps. Among these were: (1) heating the traps with a burner, rejected because of potential for trap damage and poor reliability due in part to the inability to measure soot loading; (2) heating the traps electrically, not found economical; (3) precatalyzed traps,



the use of catalyzed traps, rejected for the above-noted problem with SO<sub>3</sub> formation for precious metals and degradation for base metals; (4) the use of several fuel additives, rejected because of potential engine deposits, marginal effectiveness, and the need for an on-board reservoir and complex blending system; and (5) directly injecting a catalyst into the trap at extremely high concentrations, 0.0075 g for base metals and 0.0015 g in the case of a mixture of platinum and palladium for each 0.2 - 0.3 g of soot. In the last of these tests, they found that the use of base metals was superior to the precious metals at the levels tested and that higher levels of precious metals would be necessary for effectiveness. In another, the catalyzed trap test, they tested two types of soot in respect to the SOF and found that there was virtually no difference between the two. It now appears that these workers were led away from the best solution to the problem by these two observations.

15

Catalyzed diesel traps, of the type mentioned above, are not to be equated with triple-effect catalytic converters of the type used for gasoline engines. Triple-effect catalytic converters of this type simply don't work for diesel engines due to the different manner of operation and the different composition of exhaust gases. Reference is made to the following patent publications related to catalyst technology for gasoline engines: U. S. Patent No. 5,387,569, U. S. Patent No. 5,386,690, U. S. Patent No. 5,322,671, WO 94/22983, WO 94/22577 and WO 94/09431. In U. S. Patent No. 5,322,671, for example, a catalyst comprising platinum, rhodium or rhenium is added directly to a special catalyst chamber, meant to replace a conventional three-way catalytic converter for a gasoline engine. This patent does not address the issue of particulate emissions from diesel engines. The factors which permit the possible effectiveness of this catalytic approach for gasoline engines are very different for diesels. Gasoline engines do not run as lean as diesels, permitting the oxidation of hydrocarbons and carbon

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monoxide along with the reduction of  $\text{NO}_x$ . Moreover, gasoline engines do not produce the amount of particulates as diesel engines, and the triple-effect catalytic converters do not, therefore, suffer from particulate contamination.

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In U. S. Patent No. 5,034,020, fuel-soluble platinum additives are disclosed to provide or replenish catalyst metals on a diesel trap to facilitate burning off of trapped particulates or on a catalytic converter for a gasoline engine to maintain its activity. It is now understood, however, that while  
10 addition of the platinum group metal to the fuel before combustion may be effective for catalyzing the trap, it is not the best manner to add the catalyst for reducing the balance point of the diesel trap and achieving reductions in emissions of gaseous unburned hydrocarbons and carbon monoxide, especially where the use of auxiliary catalytic metals is  
15 contemplated.

A number of other fuel additives have been proposed for adding to diesel fuels to affect the nature of particulates deposited on diesel traps or otherwise improve the collection or disposition of the particulates. For  
20 example, U. S. Patent Nos. 4,664,677, 5,279,627, 5,348,559, 5,360,459 and 5,374,154, describe the use of copper-containing organometallic complexes which, when added to diesel fuel, tend to reduce the ignition temperature of exhaust particulates held in a diesel trap. These additives are not known to lower carbon monoxide and unburned hydrocarbons,  
25 and some tests indicate that they can increase emissions of these pollutants.

In another related teaching, U. S. Patent No. 4,458,357 describes the use of a fuel additive containing cerium and manganese to reduce the  
30 quantity of particulate material necessary to sustain combustion of the

particulates on the trap - if combustion is initiated by a glow plug. Again, this patent does not address an overall solution to the diesel emission problem.

5           In "Assessment of Diesel Particulate Control - Direct and Catalytic Oxidation", *Society of Automotive Engineers (SAE) Paper No. 81 0112*, 1981, Murphy, Hillenbrand, Trayser, and Wasser have reported that the addition of catalyst metal to particulates by introducing it as an additive to the diesel fuel (p. 5, col. 1, l. 17-20) can decrease the particulate ignition temperatures. In U. S. Patent No. 4,631,076, Kurihara, *et al.* assert that the addition of  
10           large doses of catalyst metals to the exhaust of a diesel engine will, shortly after addition, cause the built up soot to start to burn. They group platinum, palladium, copper and nickel together and do not distinguish between the various water or oil-soluble compounds. The levels used amount to 30 cc of  
15           a 1% solution. It would be desirable if much lower amounts could be used and effect lowered emissions of hydrocarbons and carbon monoxide while lowering the temperature at which the particulates on the trap could be burned by auto ignition.

20           R. W. McCabe and R. M. Sinkevitch summarized their studies of diesel traps catalyzed with platinum and lithium, both individually and in combination. (Oxidation of Diesel Particulates by Catalyzed Wall-Flow Monolith Filters. 2. Regeneration Characteristics of Platinum, Lithium, and Platinum-Lithium Catalyzed Filters; *SAE Technical Paper Series-872137*, 1987)  
25           They noted that carbon monoxide conversion to the dioxide was negligible over the lithium filter, good for platinum, but good only initially for the combined catalyst. They further noted that platinum undergoes a reversible inhibition due to the presence of SO<sub>2</sub>, but in the presence of the lithium catalyst there is apparently a wetting of the platinum crystallites by  
30           Li<sub>2</sub>O<sub>2</sub>. From this work, it can be seen that platinum and lithium on their own

help burn particulates at low temperature, but not necessarily low enough to make supplemental heat unnecessary or in a manner lowering the production of carbon monoxide and unburned hydrocarbons while the same time the balance point of the trap is reduced and maintained at low levels over extended time periods.

In a more recent report, B. Krutzsch and G. Wenninger discussed their investigation of sodium and lithium-based fuel additives. (Effect of Sodium- and Lithium-Based Fuel Additives on the Regeneration Efficiency of Diesel Particulate Filters, *SAE Technical Paper Series 922188*, 1992) They noted that the predominantly used diesel additives were based on transition metals such as iron, copper, and manganese. The transition metals were seen to form oxides which foul the traps and cannot be easily removed. They found that the sodium and lithium additives permitted regeneration at temperatures low enough to possibly eliminate the need for supplementary heat, and did, therefore, have some promise in improving trap operation as was achieved previously with the transition metal catalysts. However, they also pointed out that there was no effect on the gaseous components, thus both carbon monoxide and unburned hydrocarbon levels remained higher than would be desired.

There is a present need for an improved means for rendering the exhaust from diesel engines more environmentally benign by the use of catalysts in an effective regimen to achieve improved particulate trap regeneration along with practical gaseous pollutant reductions. More specifically, there is a need for means to reduce the temperature necessary for regenerating a particulate trap while also reducing the emissions of carbon monoxide and unburned hydrocarbons, and preferably utilizing a minimum of metals to deter trap fouling and maintain low cost. These needs are particularly acute for mobile applications, such as automobiles

and trucks used for metropolitan duty, which stress the system at extremes of operation - from low loads following start up to high-temperature, full-load conditions. And, because different engine designs are preferred among the various manufacturers for their particular engineering criteria and operating conditions, it would be desirable to provide a regimen which would permit the use of a single base fuel and supplemental treatments designated according to engine and use criteria.

## 10 Disclosure of Invention

The invention relates to improvements in reducing emissions of pollutants from a diesel engine equipped with a diesel particulate trap, by providing a method for introducing catalyst metals into the trap with the effect of reducing the balance point of the trap (the temperature at which the rate of trap loading equals the rate of regeneration) and simultaneously reducing the emissions of both unburned hydrocarbons and carbon monoxide.

The invention is based on the discovery that although the normal wide range of operating conditions of a diesel dramatically change the nature of the exhaust, in terms of the rate and degree of particulate loading, particulate composition, exhaust gas temperature at the trap, trap temperature, and gaseous unburned hydrocarbons and carbon monoxide, this need not be a hindrance to pollution control efforts where the use of catalysts is properly implemented. The catalysts include platinum group metals, preferably in combination with auxiliary catalyst metals. It is an advantage of the invention that significantly improved overall reductions of trap balance point, unburned hydrocarbons and carbon monoxide can be achieved when at least a portion of the platinum group metal catalyst is

added following combustion and at least a portion of any auxiliary catalyst used is introduced directly into the fuel prior to combustion.

5 In one embodiment, a multi-metal catalyst composition, comprising a combination of a platinum group metal catalyst and at least one auxiliary catalyst metal, is introduced into the diesel particulate trap with the hot combustion gases produced by the combustion of diesel fuel in the diesel engine, with the proviso that at least a portion of the auxiliary catalyst metal is added to the diesel fuel and at least a portion of the platinum group  
10 metal is added directly to the hot combustion gases following combustion. Preferably, the platinum group metal catalyst and the auxiliary catalyst metal will be in the form of diesel-fuel-soluble organic compounds or complexes. Platinum group metals include platinum, palladium, rhodium, ruthenium, osmium, and iridium. Compounds including platinum,  
15 palladium, and rhodium, especially compounds of platinum alone or in combination with rhodium and/or palladium compounds are preferred in the practice of this invention since the vapor pressure of these metals is sufficiently high to facilitate the desired reduction of carbon monoxide emissions.

20

As will become apparent from the following detailed description, it is also preferred that the platinum group metal catalyst be introduced into the exhaust with a combustible organic liquid, preferably as a diesel-fuel-soluble compound or complex. The platinum group metal catalyst is  
25 introduced, in total, in an amount effective to provide less than one part by weight of platinum group metal per million parts by volume fuel (ppm) based on the volume of fuel burned to produce the exhaust gases. More preferred concentrations are within the range of from 0.05 to 0.5 ppm, e.g., from about 0.1 to about 0.3ppm. For the purposes of this description, all  
30 "parts per million" figures are on a weight-to-volume basis, i.e., grams/million



cubic centimeters (which can also be expressed as milligrams/liter), and all percentages are given by weight, unless otherwise indicated.

When employed, the auxiliary catalyst metal will include one  
5 selected from the group consisting of compounds of sodium, lithium, potassium, calcium, magnesium, cerium, iron, copper, manganese, and mixtures of these. The auxiliary catalyst metal composition can be employed to deliver the auxiliary catalyst metal at suitable levels, e.g., from about 1 to about 100 ppm and preferably 20 to 60 ppm of the catalyst  
10 metal in combination with the platinum group metal composition in diesel fuels. It is preferred to add all of the auxiliary catalyst metal to the fuel in amounts effective to, in combination with the platinum group metal catalyst, to reduce the balance point temperature of the trap by at least 50°C, and preferably by at least 150°C.

15 In another embodiment, the use of an auxiliary catalyst metal is not required, and the platinum group metal catalyst is introduced, at least in part, in suitable form directly into the hot combustion gases following combustion. Preferably, an auxiliary catalyst metal will be employed in the  
20 form of a diesel-fuel-soluble organic compound or complex.

### Description of the Drawings

25 The invention will be better understood and its advantages will be more apparent when the following detailed description is read in light of the accompanying drawings, wherein:

30 Figure 1 is a schematic view of an embodiment of the invention wherein a catalyst composition is introduced directly into the exhaust gas after exit from the combustion chamber of a diesel engine;



Figure 2 is a schematic view similar to that of Figure 1, but additionally showing introduction of a catalyst composition as a fuel additive to the fuel line downstream of the fuel tank; and

Figure 3 a schematic view similar to that of Figure 2, but showing introduction of a catalyst composition into the combustion air upstream of the diesel engine combustion chambers.

#### Detailed Description of Preferred Embodiments

In this description, the term "diesel engine" is meant to include any of those engines capable of running on "diesel fuel", as defined by the American Society of Testing and Management (ASTM) Standard Specification for Fuel Oils (designation D 396-86) or any of grade numbers 1-D, 2-D or 4-D, as specified in ASTM D 975. More generally, diesel fuel can be a fuel oil No. 2 or No. 4 petroleum distillates as well as alternative diesel fuels containing emulsified water or alcohols such as ethanol or methanol, very low sulfur fuels (less than 0.05% sulfur), diesel fuel blends with bioderived components (animal and vegetable fats and oils, fractions and derivatives), and the like, as long as they exhibit volatility and cetane number characteristics effective for the purpose. Diesel fuels will typically have a 90% distillation point within the range of 300° to 390°C and a viscosity of from 1 to 25 centistokes at 40°C.

The invention concerns diesel engines equipped with or having associated therewith diesel engine particulate traps. By this it is meant that a diesel engine particulate trap is disposed such that the exhaust stream from the engine passes therethrough. Generally, a diesel engine

particulate trap (also referred to herein as a "diesei trap") is disposed in the exhaust system, typically on the tailpipe of the vehicle in which the diesel engine is located, downstream from the exhaust manifold. It can be positioned upstream or downstream of the point that exhaust is withdrawn for recirculation for NO<sub>x</sub> control, if that option is adopted.

Suitable diesel traps are known to the skilled worker and generally comprise an apparatus designed to trap or collect particulates present in the exhaust stream of the diesel engine. Such a trap can be made of any suitable material such as ceramic (for instance, a cordierite ceramic material), glass fiber, or metal. In addition, the trap can be coated with a catalytic material to facilitate regeneration. It is an advantage of the present invention that the traps are selectively catalyzed during operation.

Flow resistance to the exhaust increases in proportion to the efficiency of the diesel trap at collecting particulates, and a compromise must be made between trap efficiency and exhaust back pressure. One type of diesel engine particulate trap which is effective at trapping particulates while still providing an acceptable compromise in terms of back pressure created, includes traps available under the trademarks Diesel filter and EX 51 100/17 from Corning Glass Corporation of Corning, New York.

Diesel engine particulate traps typically include a gas permeable structure made of a suitable material, such as a ceramic. Traps can be configured to include at least two (and generally several) parallel gas channels longitudinally arranged in a honeycomb-type structure extending between what can be referred to as an upstream, or engine-side, face and a downstream, or exhaust-side, face. Each passage is plugged at one of its faces such that alternate faces of adjacent passages are plugged. In this

way, exhaust entering the trap through a passage at its unplugged upstream face must pass through a wall into an adjacent passage in order to exit the trap from its unplugged downstream face. Particulates in the exhaust are then trapped or collected on the wall. Such a trap is described, for instance, in U.S. Patent 4,568,357 to Simon, the disclosure of which is incorporated herein by reference.

Particulate traps used in the methods of the invention are preferably capable of withstanding the rigors of self regeneration. That is, the traps will retain structural and functional integrity when trapped particulates are ignited therein by heat derived from the engine, usually from the hot exhaust gasses themselves, aided by the catalysts introduced according to the invention. In order to reduce particulate buildup on the trap, it is desired that the particulates are combusted or "burned off" the trap in order to free the surface thereof for further collection of particulates and maintenance of a low average back pressure.

Under normal conditions and without the use of a catalyst, temperatures of from over about 500°C up to about 600°C, and sometimes more, are required to combust the particulates and, thus, regenerate the trap. Since a four-stroke diesel engine produces combustion gases which are typically exhausted at an average temperature of between about 400°C and 500°C, and which only occasionally reach temperatures in excess of 600°C, the exhaust gas temperature is too low to lead to reliable trap regeneration. And, despite the attainment of the periodic high temperatures, the particulates produced by four-stroke diesels are relatively low in SOF and ignite with difficulty. A two-stroke diesel engine produces exhaust gases at an even lower temperature, which rarely exceeds 600°C, making reliable trap regeneration even less likely without the use of a catalyst.

The invention improves the operation of diesel engines equipped with traps, either catalyzed or uncatalyzed, and if catalyzed in any stage of activity. In each of the embodiments of the invention, the regeneration characteristics of the trap are improved by lowering the balance point of the trap. In other words, the invention lowers the temperature of the trap whereat a steady state is achieved and the rate of particulate deposit in the trap is the same as the rate of particulate burning in the trap. Thus, at the balance point (temperature), the trap is regenerated at the same rate that it is loaded. The balance point can be determined by plotting against temperature, the incremental change in temperature divided by the incremental change in pressure through the trap. The temperature at the point where the plotted line crosses the abscissa, can be taken as the balance point and is used to define that term for the purposes of this description.

The invention enables the balance point to be lowered sufficiently to permit reliable trap regeneration, and to do so with reductions in carbon monoxide and unburned hydrocarbons. The art has not previously been able to achieve such significant results in these apparently contradictory effects. It is an advantage that, in the preferred embodiment, no auxiliary heater is needed to achieve continuous regeneration during sustained operation of the diesel engine. It is also an advantage of the invention that the benefits achievable for the platinum group metals (including reductions in hydrocarbons, carbon monoxide, and trap balance point temperature) are not adversely affected by the presence of auxiliary catalysts, making it possible to obtain the positive benefits of both the platinum group metal catalyst and the auxiliary catalyst.

It is an advantage of the invention that when the platinum group metal is added, at least in part, to the combustion gases downstream of the

combustion chamber, the particulates produced tend to have more SOF of proper composition relative to the carbon core (or the total particulate weight) than when the platinum group metal is added to the fuel. This has a highly beneficial effect on the balance point. On the other hand, it is an advantage of the invention that the use of an auxiliary metal catalyst in the fuel will tend to further provide a desirable SOF proportion in the particulates. In the case of copper, the solids tend to be richer in SOF while in the case of cerium the particulates tend to be smaller with a desirable SOF fraction. The invention advantageously utilizes these advantages to provide a treatment regimen that not only permits the achievement of a reduced trap balance point with reduced hydrocarbon and carbon monoxide emissions, but it permits the easy variation of the treatment from manufacturer to manufacturer.

In furtherance of the attainment of these advantages, it is preferred that the catalysts be added in amounts, in compositions, and at the locations effective to maintain the soluble organic fraction at an amount of at least 25% by weight of the particulates, and preferably at an amount of at least 40% by weight of the particulates. An individual engine manufacturer will define performance curves for its engines and recommend treatment regimens consistent with the invention to permit control of trap regeneration, and it will accomplish this at very low dosages relative to particulates produced, without the expected increase in hydrocarbon and carbon monoxide emissions.

25

It is an advantage of one embodiment, that the combinations of particulate traps and the catalyst materials added in accord with the invention, can be employed along with a known technique for controlling NO<sub>x</sub> emissions, such as exhaust gas recirculation or retarding engine timing, without suffering the penalties normally associated with these techniques.

30



In this manner, the combined emissions of HC, CO, NO<sub>x</sub> and particulates are reduced from what is possible with current technology.

5 The platinum group metal catalyst compositions can be of any composition effective to deliver the catalyst metal to the diesel trap. Thus, they can be of a type which is soluble in nonpolar hydrocarbon fuels, soluble in polar fuels such as those including methanol, ethanol, or other lower alkyl alcohols, soluble in fuels having polar and nonpolar components such as emulsified fuels and gasohol, or soluble in water or other suitable  
10 vehicle for introduction into the intake air or the exhaust gases. In any of these forms, the platinum group metal catalyst can be made available by contact with hot combustion gases, either during combustion or in the exhaust system, to reduce the balance point of the trapped particulates and the emission of gas-phase hydrocarbons and carbon monoxide from  
15 the trap.

It has been determined according to the present invention, that these results will be best achieved when at least a portion of the platinum group metal catalyst, preferably at least 50% of the amount employed, is  
20 added directly to the exhaust gases downstream of the diesel engine. Also preferably, this catalyst will be introduced with an organic liquid. And, it is preferred that an auxiliary catalyst metal composition, preferably of copper or cerium, be introduced into the fuel prior to combustion.

25 Figure 1 illustrates a diesel engine 10 having an exhaust manifold 12 directing the exhaust from the engine to an exhaust system including a diesel trap 20 and a tail pipe 30. The diesel engine is supplied with fuel from tank 40 via line 42 and fuel injectors 44, 44', 44'', and 44'''. The fuel tank includes diesel fuel and can include a preferred, optional auxiliary catalyst  
30 metal as will be described in detail below.



The auxiliary catalyst metal can be supplied from a separate canister (not shown) fitted to the fuel line or from a suitable supply vessel such as 60 via line 62 shown in Figure 2. If desired, the fuel can also include a minor portion of a platinum group metal catalyst, although it is preferred according to the invention to introduce at least half, preferably all, of the platinum group metal catalyst into the hot exhaust gases following combustion. The embodiment of Figure 3 shows a vessel 70 and a line 72 for feeding a suitable catalyst composition, e.g., a platinum group metal composition such as those in water-soluble or water-dispersible forms, into the intake air line 14. Again, however, for the embodiment of Figure 3, it is preferred that at least 50% of the total platinum group metal be added to the combustion gases downstream of the combustion chambers of the engine.

Each of these embodiments enables and is controlled in a manner effective to progressively load the platinum group metal catalyst, and preferably an auxiliary catalyst metal, onto the diesel trap in intimate contact with the particulate matter as it is collected in the trap 30. This enables reduction of the balance point (temperature) for trap regeneration, and done in accord with the regimen of the invention, reduces gaseous hydrocarbons and carbon monoxide.

The regimen of the invention requires the introduction of from 0.05 to 1 ppm of a platinum group metal catalyst (based on the volume of fuel combusted) into the particulates, by introducing at least half of the platinum group metal catalyst directly into the hot exhaust gases. Preferably, the platinum group metal catalyst is employed with a combustible organic liquid to aid in either progressively loading the trap with combustible organics or to combust in the hot combustion gases to facilitate burning of the particulates on the trap for more effective

regeneration. The judicious selection and use of an auxiliary catalyst metal, preferably adding at least half of its total to the fuel as a fuel additive, is a preferred part of the regimen to achieve the lowest trap balance point.

- 5       The primary control system for introducing the platinum group metal catalyst will be to meter it in direct proportion to either sensed or programmed fuel flow to achieve the desired use levels. Metering in this manner can be either continuous (preferred) or intermittent to achieve the desired loading of catalyst metal and, preferably, also a combustible  
10       organic liquid employed as a vehicle for the catalyst composition. It will be understood that burning of the particulates in the trap is accompanied by an increase in trap temperature and exhaust from the trap, and a decrease in back pressure. Control can thus be related to measured changes in either parameter, and increased dosages over those  
15       determined based on fuel flow, can be introduced.

      The platinum group metal catalyst compositions can be formulated as known to the art to have the degree of stability necessary to assure that the platinum group metal catalyst composition survives storage and  
20       handling, despite the presence of water or excessive heat, to release the platinum group metal catalyst into the exhaust gases. Release of the platinum group metal catalyst from any compound or carrier composition can occur either during combustion of the air-fuel mixture in the cylinder, if the catalyst composition is added to either the fuel (Figures 1 or 2) or the  
25       combustion air (Figure 3), or decomposition in the hot exhaust gases in the case where the catalyst composition is added to the hot combustion gases downstream of the combustion chamber. In either case, the active catalyst metal is transported to the exhaust system wherein it is deposited in the trap along with the particulates and any auxiliary catalyst metal.

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Line 24 supplies combustion air to the combustion chambers (not shown) of the diesel engine. If desired, a portion of exhaust gas from line 12 or line 30 can be recirculated into line 14 as is known in the art for exhaust gas recirculation. The amount of exhaust gases recirculated in this embodiment will be effective to lower the production of  $\text{NO}_x$  by the engine utilizing the combustion air mixture as compared to combustion air not containing exhaust gases. Typically, from about 1 to about 20% can be efficiently recirculated. This normally lowers the production of  $\text{NO}_x$  but results in increased production of particulates, unburned hydrocarbons and carbon monoxide.

Upon introduction and compression of the combustion air (this term including air alone or a mixture of fresh air and recirculated exhaust gases) in the cylinders of the diesel engine, diesel fuel is injected into the cylinders at the appropriate point in the timing of the combustion cycle to form and combust a fuel-air mixture. The fuel-air mixture in the cylinders typically has an excess oxygen content of from about 2 to about 15%.

In another aspect of the invention,  $\text{NO}_x$  can be reduced by setting the injection timing of a diesel engine (for instance retarded or set during manufacture of the engine). Preferably, injection timing can be retarded by between about  $0.5^\circ$  and about  $8^\circ$  to secure the advantages of the invention. More particularly, the engine timing can be retarded between about  $2^\circ$  and about  $6^\circ$  in order to achieve satisfactory reductions in nitrogen oxides levels. If, for example, the injection timing is initially set at  $18^\circ$  before top dead center, practice of this aspect of the invention dictates that it is preferably retarded, by which is meant injection occurs closer in time to top dead center, to about  $17.5^\circ$  to about  $10^\circ$ , more preferably about  $16^\circ$  to about  $12^\circ$ , before top dead center.

The injection timing should be set at that level sufficient to reduce nitrogen oxides emissions to a predetermined level, such as required by regulatory authorities. For instance, in some jurisdictions, it is required that diesel engines (notably new engines) emit no more than 4 grams per brake horsepower-hour (gm/BHP-hr) of nitrogen oxides. Although not always possible, reduction of NO<sub>x</sub> levels to no greater than about 4 gm/BHP-hr is desired whether by the use of exhaust gas recirculation or modification of engine timing.

The platinum group metal catalyst compositions can be fuel-soluble, fuel-soluble but water-sensitive, or water-soluble, as will be described below. The platinum group metal catalyst compositions are typically added in amounts effective to provide concentrations of the platinum group metal relative to the fuel of less than 1 part per million (ppm). When employed, the auxiliary catalytic metal compositions are preferably used in amounts to provide concentrations of from about 1 to about 100 ppm of the metal.

The platinum group metal catalyst is employed in a total amount effective upon combustion of the diesel fuel to provide sufficient platinum group metal in the exhaust system to lower the emissions of unburned hydrocarbons and carbon monoxide. This will be less than about 1 ppm, based on the weight of the catalyst metal and the amount of diesel fuel combusted. Preferably it will be within the range of from about 0.05 to about 0.5 ppm, and most preferably in the range of from 0.10 to 0.30 ppm, on this basis.

#### **Fuel-Soluble Platinum Group Metal Catalyst Compositions**

Preferred among the platinum group metal catalyst compositions are those which are soluble in a nonpolar organic liquid such as diesel fuel or

mineral spirits, or any other essentially nonpolar hydrocarbon. These materials are preferred according to the present invention because they can be stored for long time periods and resist minor amounts of water contamination and moderate thermal abuse, and yet degrade in contact with hot combustion gases to provide both the platinum group metal catalyst and additional combustible organics. The use of compounds of this type with suitable organic liquids such as diesel fuel or mineral spirits, in amounts providing a ratio of catalyst metal to organic liquid of from about 1:25 to about 1:25,000.

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At relatively low exhaust gas temperatures, these additional organic liquids will not immediately burn in the exhaust gases, but will progressively load the trap with easily combustible material to aid in the autoignition of the particulates by the platinum group catalyst alone or with an auxiliary catalyst metal. At higher exhaust gas temperatures, they will tend to at least partially combust and increase the temperature of the exhaust gases so that autoignition is facilitated. In both of these cases, the use of a combustible organic liquid injected into the exhaust stream is beneficial to the reduction of the trap balance point, but does not – due to the simultaneous introduction of platinum group metal catalyst prior to the diesel trap – exhibit the expected problem of increasing the discharge of hydrocarbons and carbon monoxide.

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Among these preferred platinum group metal catalyst compounds are hydrocarbon-fuel-soluble organometallic platinum group metal coordination compounds. The compounds in this group are any of those disclosed for example in prior U.S. Patent Nos. 4,892,562 and 4,891,050 to Bowers and Sprague, 5,034,020 to Epperly and Sprague, 5,215,652 to Epperly, Sprague, Kelso and Bowers, and 5,266,083 to Peter-Hoblyn, Epperly, Kelso and Sprague, and WO 90/07561 to Epperly, Sprague, Kelso and

25  
30



Bowers. Each of these patents and applications is incorporated by reference to illustrate representative compounds of the fuel-soluble type. Reference can be made to these disclosures for details of preparation and purification. Where the application permits, a blend of these compounds  
5 can be used with one or more other platinum group metal compounds such as soaps, acetyl acetonates, alcoholates,  $\beta$ -diketonates, and sulfonates, e.g., of the type which will be described in more detail below. Preferably, the composition will be temperature stable, and substantially free of phosphorus, arsenic, antimony, or halides.

10  
Advantageously, in fuels or systems where some tramp water may be present, the platinum group metal catalyst composition will also be substantially insensitive to water, as evidenced by a partition ratio sufficient to maintain significant preferential solubility in the fuel. The relative solubility  
15 of the composition in the diesel fuel and water is important since there is often a substantial amount of water admixed in with fuel, and any platinum group metal catalyst composition which separates from the fuel can precipitate out or be lost as a coating on fuel system walls. The relative solubility of the composition in the fuel is referred to herein as the "partition  
20 ratio" and can be expressed as the ratio of the amount in milligrams per liter of composition which is present in the fuel to the amount which is present in the water. This can most easily be determined in a 100 milliliter (ml) sample which is 90% fuel and 10% water. By determining the amount of composition in the fuel and the amount in the water, the partition ratio can  
25 be readily determined.

The organic nature of the platinum group metal compositions of this type provides solubility in nonpolar hydrocarbon fuels such as diesel fuel, thereby facilitating the introduction of the composition into the combustion  
30 chamber of an internal combustion engine. High fuel solubility maintains



the platinum in the fuel and inhibits its precipitation or plating out in vessel 50 or line 52, or in a fuel tank or fuel lines in the case where a minor portion of it is introduced into the combustion chamber. In uses where the composition is intended for long-term storage either as a concentrate or with a fuel or fuel oil, high fuel solubility and stability in solution are important. In uses where the composition as part of an additive is mixed with the fuel shortly before introduction into the engine, a lesser stability can be effective.

Temperature stability of the composition is important in many practical and operational contexts. Typically, the breakdown temperature of the platinum group metal catalyst composition should be at least about 40°C, preferably at least about 50°C, in order to protect against most temperatures to which it can be expected to be exposed. In some circumstances, it will be necessary that the breakdown temperature be no lower than about 75°C.

The preferential solubility of the composition in fuel as compared to water can be critical because if a substantial amount of the composition is dissolved in the water which may be present, the overall effectiveness of the composition is proportionally reduced. This partition ratio should be at least about 25 and is most preferably greater than about 50. In order to reduce the water susceptibility of the platinum group metal catalyst composition, the composition can have at least one platinum group metal-to-carbon covalent bond. A platinum group metal-to-oxygen or platinum group metal-to-nitrogen bond can be acceptable, but there must also be at least one metal to carbon bond.

### Water-Sensitive and Water-Soluble Platinum Group Metal Catalyst Compositions

In addition to the highly fuel-soluble compounds that are stable in the presence of water, the invention makes use of platinum group metal catalyst compositions which would normally be taken up or destabilized by any water present. These platinum group metal catalyst compositions can be either simply water-sensitive or essentially water-soluble the formulation and use of which is described in detail in U. S. Patent Application Serial No. 08/372,188, filed January 13, 1995, by the inventors of the present application, the entire disclosure of which is hereby incorporated by reference.

Water-sensitive platinum group metal catalyst compositions are characterized as being unstable in the presence of from about 0.01 to about 0.5% water, but having sufficient affinity for the fuel that when a water-functional composition is employed, they remain in the fuel and effective for their intended catalytic function. Among the platinum group metal catalyst compositions in this group are, alcoholates, sulfonates, substituted and unsubstituted beta-diketonates and soaps selected from the group consisting of stearates, palmitates, laurates, tallates, naphthanates, other fatty acid soaps, and mixtures of two or more of these.

The water-sensitive compounds typically exhibit partition ratios of from about less than 50, down to about 1. Compositions of this type having partition ratios as low as 40 and below, e.g., less than 25, and more narrowly

less than 1 to 20, can be effective according to the invention. Also, essentially water-soluble platinum group metal catalyst compositions having partition ratios of less than 1 can be employed according to the invention.

5 To achieve stability in the presence of water, the catalyst-containing compositions are formulated to include a water-functional composition selected from the group consisting of lipophilic emulsifiers, lipophilic organic compounds in which water is miscible, and mixtures of these, which can be added to the fuel as an additive including any catalyst compositions, as a  
10 discrete additive or as part of the bulk fuel. The preferred compounds or compositions have the capability of preventing frank separation of water from the fuel and maintain it tied up in the fuel, preferably in complete miscibility with a nonpolar fuel component or in stable, dispersed droplets.

15 In addition to the materials described above and in U.S. Patent No. 4,891,050 to Bowers, *et al.*, U.S. Patent No. 5,034,020 to Epperly, *et al.*, and U.S. Patent No. 5,266,083 to Peter-Hoblyn, *et al.*, other platinum group metal catalyst compositions include commercially-available or easily-synthesized platinum group metal acetylacetonates, platinum group metal  
20 dibenzylidene acetonates, and fatty acid soaps of tetramine platinum metal complexes, e.g., tetramine platinum oleate. In addition, there are the water soluble platinum group metal salts such as chloroplatinic acid, sodium chloroplatinate, potassium chloroplatinate, iron chloroplatinate, magnesium chloroplatinate, manganese chloroplatinate, and cerium  
25 chloroplatinate, as well as any of those compounds identified or included within the description set forth by Haney and Sullivan in U. S. Patent No. 4,629,472.

### Auxiliary Catalyst Metal Composition

In the most preferred embodiment, an auxiliary catalyst metal is added to the fuel. Preferably, at least 50% of the auxiliary catalyst metal will be added to the fuel in the form of a fuel-soluble composition and released into the hot combustion gases when the fuel is burned in the combustion chamber. Among the useful metallic compositions are organometallic salts of manganese, magnesium, calcium, iron, copper, cerium, sodium, lithium and potassium, which can be employed at suitable levels, e.g., from about 1 to about 100 ppm and preferably 20 to 60 ppm of the catalyst metal in combination with the platinum group metal catalyst in diesel fuels. Among these are the alcoholates, sulfonates, beta-diketonates and soaps, e.g., selected from the group consisting of stearates, palmitates, laurates, tallates, naphthanates, other fatty acid soaps, and mixtures of two or more of these, of copper, calcium, magnesium, manganese, iron, cerium, sodium, lithium and potassium compounds as are known as fuel soluble and useful fuel additives.

Some catalyst metals, such as set forth in the above citations, are known as useful for reducing the temperature at which diesel traps can be regenerated. However, unlike the prior art, the invention permits them to achieve their known function while the emissions of hydrocarbons and carbon monoxide are reduced. Moreover, the invention reduces the balance point sufficiently low to permit NO<sub>x</sub> reduction by modifying engine timing or exhaust gas recirculation without the concern for increased particulates which would normally be associated with those techniques.

Among the lithium and sodium compounds are organometallic compounds and complexes as well as the salts of lithium and sodium respectively, with suitable organic compounds such as alcohols or acids,

e.g., aliphatic, alicyclic and aromatic alcohols and acids. Exemplary of particular salts are the lithium and sodium salts of tertiary butyl alcohol and mixtures of these. Other lithium and sodium organic salts are available and suitable for use to the extent that they are fuel-soluble and are stable in solution. While not preferred, inorganic salts can also be employed to the extent that they can be efficiently dispersed in the fuel, such as in a stable emulsion or otherwise.

Among the specific sodium compounds are: the salts of sulfonated hydrocarbons, for example sodium petroleum sulfonate, available as Sodium petronate from Witco Chemical ( $\text{NaO}_3\text{SR}$ ,  $\text{R} = \text{alkyl, aryl, arylalkyl}$ , and  $\text{R}$  is a hydrocarbon having greater than three carbons); sodium alcoholates, for example sodium t-butoxide and other fuel-soluble alkoxides ( $\text{NaOR}$ , wherein  $\text{R}$  is an alkyl, e.g., from 3 to 22 or more carbons; and sodium naphthenate (sodium salts of naphthenic acids derived from coal tar and petroleum). Among the specific lithium compounds are the lithium analogs of the above sodium compounds.

Among the specific cerium compounds are: cerium III acetylacetonate, cerium III naphthenate, and cerium octoate and other soaps such as stearate, neodecanoate, and octoate (2-ethylhexoate). Many of the cerium compounds are trivalent compounds meeting the formula:  $\text{Ce}(\text{OOCR})_3$ , wherein  $\text{R} = \text{hydrocarbon}$ , preferably  $\text{C}_2$  to  $\text{C}_{22}$ , and including aliphatic, alicyclic, aryl and alkylaryl.

Among the specific copper compounds are: copper acetylacetonate, copper naphthenate, copper tallate, and copper soaps of  $\text{C}_4$  to  $\text{C}_{22}$  fatty acids, including stearate, laurate, palmitate, octoate, neodecanoate and mixtures of any of these. Fatty acids for these compounds can be derived from any animal or vegetable fat or oil, or



fraction thereof, as well as from mineral oils. These copper compounds are divalent compounds, with the soaps meeting the formula:  $\text{Cu}(\text{OOCR})_2$ . In addition, complexes formed by reacting or otherwise contacting copper compounds with various organic substrates to form a organometallic  
5 complexes as disclosed by patents such as U. S. Patent No. 4,664,677, U. S. Patent No. 5,279,627, U. S. Patent No. 5,348,559, U. S. Patent No. 5,360,549, U. S. Patent No. 5,376,154, International Publication Number WO 92/20764, and the various references cited in them, can be employed.

10 Among the specific iron compounds are: ferrocene, ferric and ferrous acetyl-acetonates, iron soaps like octoate and stearate (commercially available as Fe(III) compounds, usually), iron pentacarbonyl  $\text{Fe}(\text{CO})_5$ , iron naphthenate, and iron tallate.

15 Among the specific manganese compounds are: methylcyclopentadienyl manganese tricarbonyl ( $\text{CH}_3\text{C}_5\text{H}_4\text{MN}(\text{CO})_3$ ), as described for example in U. S. Patent No. 4,191,536 to Niebylski; manganese acetylacetonate, II and III valent; soaps including neodecanoate, stearate, tallate, naphthenate and octoate.

20 The calcium and magnesium compounds can have the same anions as the copper compounds, but will also include a wider range of sulfonates and overbased sulfonates.

25 The auxiliary catalyst metal compositions are preferably included in a fuel additive composition which will preferably include a solvent which is soluble in the fuel. The fuel additive compositions may also contain other additives, such as detergents, antioxidants, and cetane improvers such as octyl nitrate which are known as beneficial to engine performance, but the  
30 use of such is not an essential feature of the invention.



The total amount of solvent and other additives used will depend on the dosage of platinum group metal catalyst composition required and on what is a convenient concentration to handle relative to the amount of fuel to be treated. Typically, solvent (plus other like additive) volumes of about  
5 0.1 to about 40.0 liters/gram of platinum are acceptable.

The above description is for the purpose of teaching the person of ordinary skill in the art how to practice the present invention, and it is not intended to detail all of those obvious modifications and variations of it  
10 which will become apparent to the skilled worker upon reading this description. It is intended, however, that all such obvious modifications and variations be included within the scope of the present invention which is defined by the following claims. The claims cover the indicated components and steps in all arrangements and sequences which are effective to meet  
15 the objectives intended for the invention, unless the context specifically indicates the contrary.

## CLAIMS

1. A method for improving the operation of a diesel engine equipped with a diesel trap, comprising:
  - combusting a diesel fuel-air mixture in a diesel engine to produce hot combustion gases;
  - introducing a platinum group metal catalyst composition into the hot combustion gases in the exhaust system of the diesel engine in an effective amount to lower the emissions of unburned hydrocarbons and carbon monoxide and to lower the temperature at which particulates are burned from the trap.
2. A method according to claim 1 wherein platinum group metal catalyst is present in the fuel in amounts effective to reduce the balance point temperature of the trap by at least 50°C.
3. A method according to claim 1 wherein the platinum group metal catalyst composition is employed at a level sufficient to supply 0.05 to about 1.0 ppm of platinum group metal based on the fuel combusted.
4. A method of claim 1 wherein said diesel engine is modified by retarding engine timing or recirculating exhaust gas effectively to reduce NO<sub>x</sub> emissions.
5. A method according to claim 1 wherein said platinum group metal catalyst composition is an alcoholate, sulfonate, beta-diketonate or a soap selected from the group consisting of stearates, palmitates, laurates, tallates, naphthanates, other fatty acid soaps, and mixtures of two or more of these.
6. A method of claim 1 wherein an auxiliary catalytic metal composition is

added to the fuel in an amount effective to provide auxiliary catalyst metal in the exhaust system to lower the balance point of the trap.

7. A method according to claim 6 wherein said platinum group metal catalyst composition is a fuel-soluble composition and is employed at a level sufficient to supply 0.05 to about 1.0 ppm of platinum group metal, and the auxiliary catalytic metal composition is employed in the fuel in an amount to provide a concentration of from about 1 to 100 ppm cerium, both concentrations based on the volume of fuel burned.

8. A method for according to claim 5 wherein said auxiliary catalytic metal composition contains at least one metal selected from the group consisting of calcium, magnesium, manganese, iron, sodium, lithium, potassium, and mixtures thereof.

9. A method for according to claim 8 wherein said auxiliary catalytic metal composition contains copper or cerium.

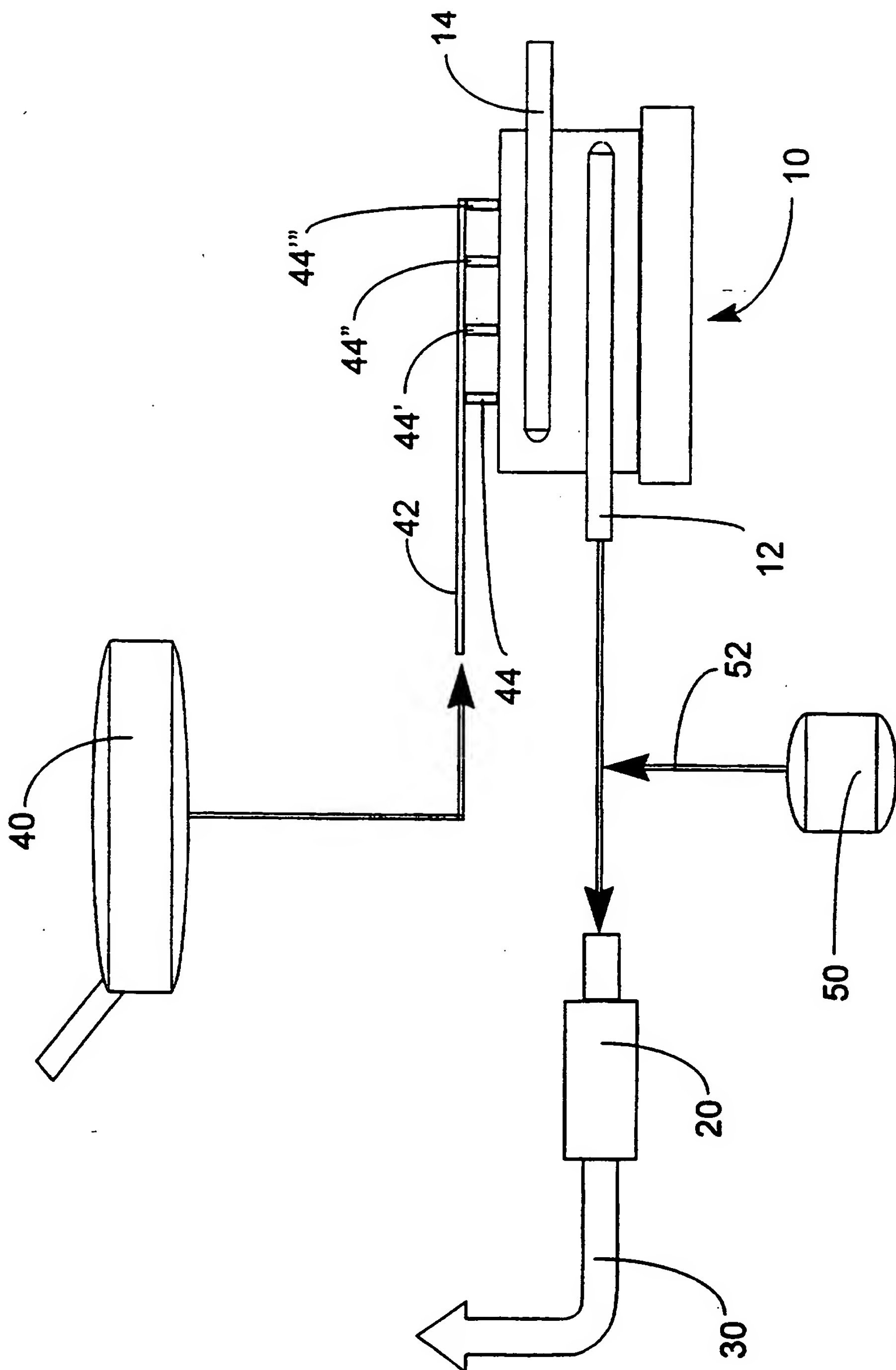
10. A method according to claim 9 wherein the platinum group metal catalyst composition is employed at a level sufficient to supply 0.05 to 1.0 ppm of platinum group metal and the auxiliary catalyst metal composition is employed at a level effective to supply from 1 to 100 ppm of the auxiliary catalyst metal, based on the fuel combusted.

11. A method of claim 10 wherein said platinum group metal composition has a breakdown temperature of at least about 50°C, a partition ratio of said platinum metal composition of at least about 25, and is introduced with a combustible organic liquid.

12. A method of claim 11 wherein at least half of the platinum group metal catalyst is introduced directly into the hot exhaust gases.

13. A method of claim 11 wherein at least half of the auxiliary catalyst metal is introduced into the fuel prior to combustion.

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**FIG. 1**

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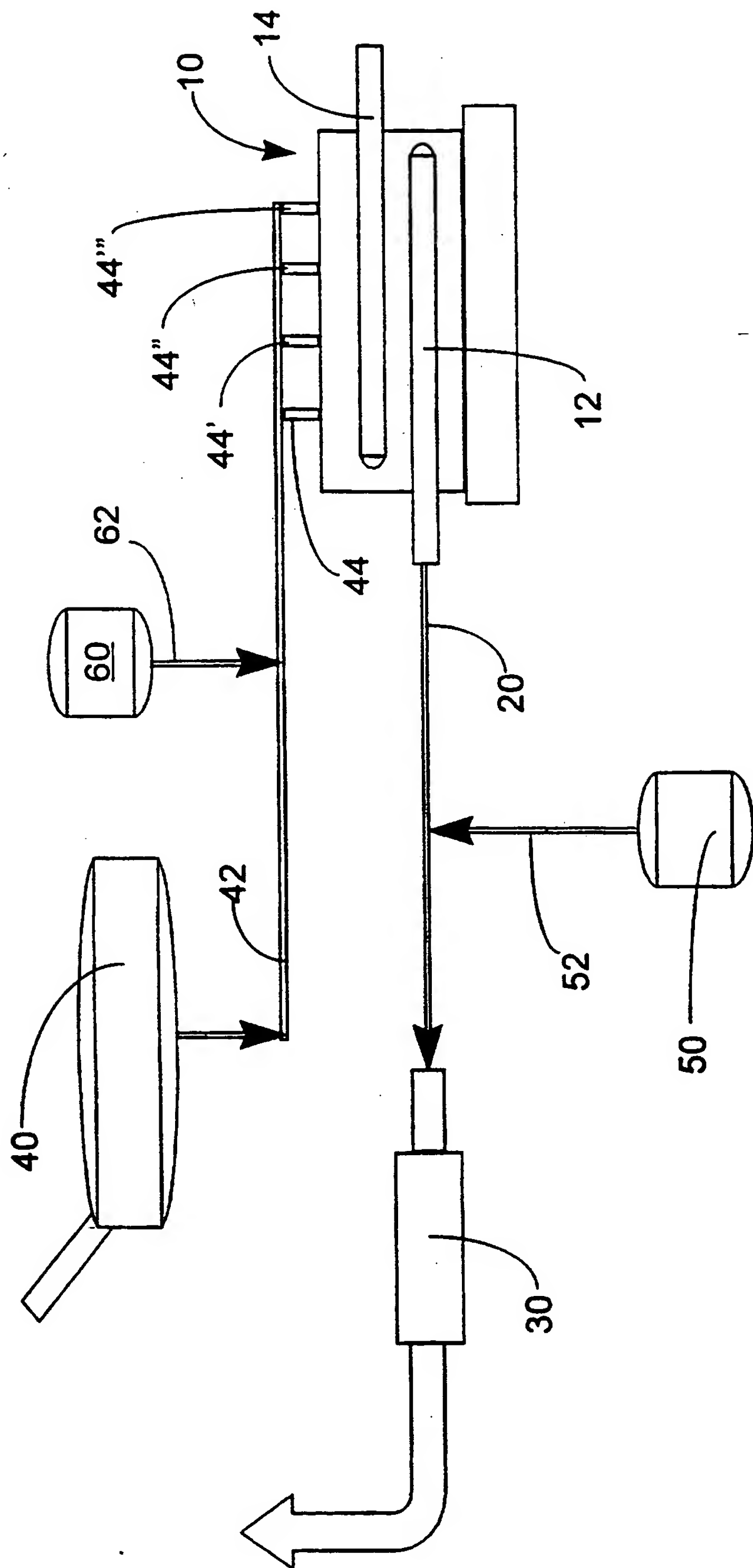


FIG. 2



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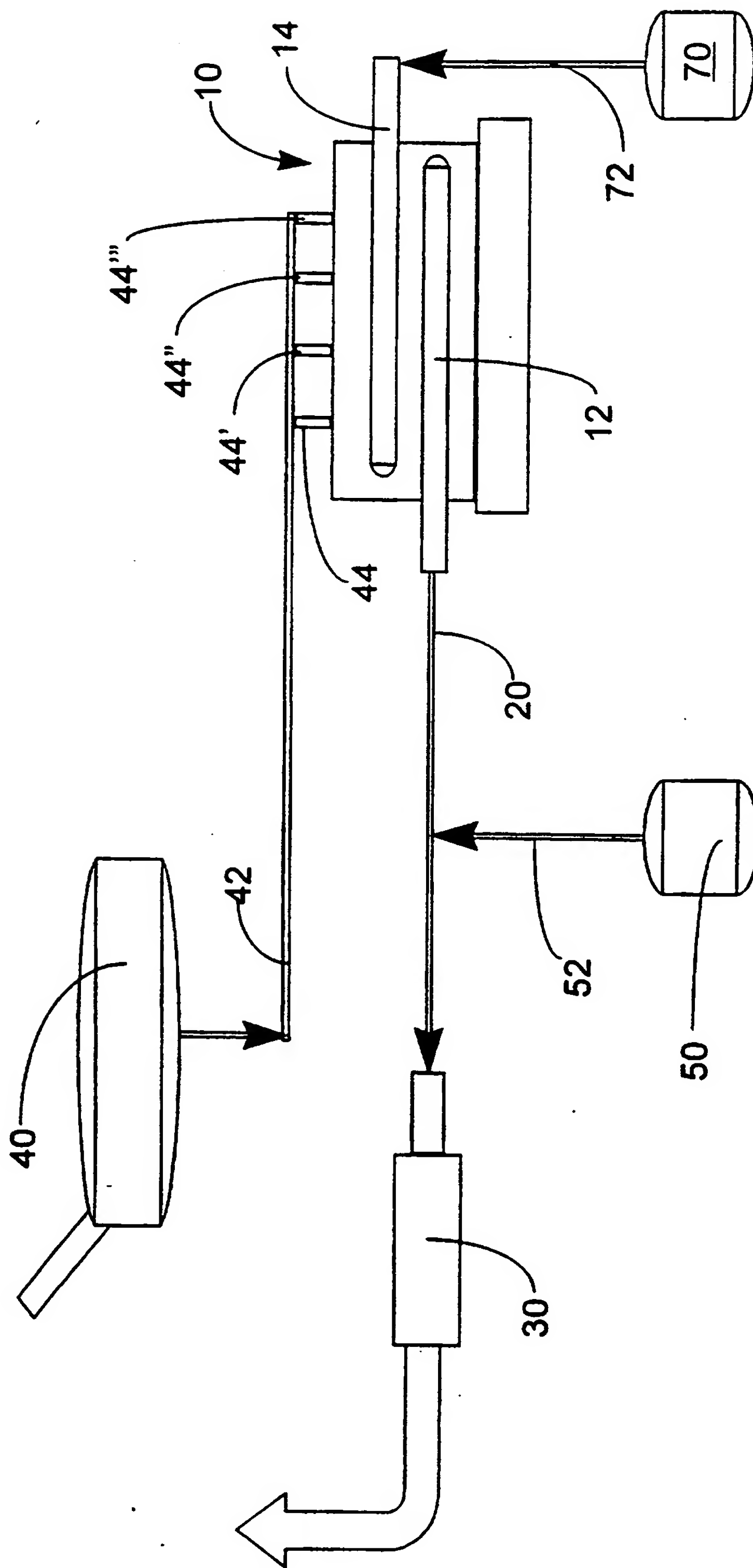


FIG. 3

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/01606

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : F01N 3/28; C10L 1/12, 1/30

US CL : 60/274, 295 AND 301; 44/354, 357 AND 358

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 60/274, 295 AND 301; 44/354, 357 AND 358

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
APS

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,266,083 A (PETER-HOBLYN et al) 30 November 1993, col. 8, lines 48-56; and col. 9, line 15 through col. 11, line 8.	1-6 --- 1-13
Y	US 4,631,076 A (KURIHARA et al) 23 December 1986, fig. 3 and col 2, lines 11-23; col. 4, examples 1 and 2.	1-13
Y	US 5,386,690 A (SHUSTOROVICH et al) 07 February 1995, fig. 2; col. 2, line 60, through col. 3, line 41.	1-13

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

22 JUNE 1997

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